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PRODUCTION OF GASEOUS RADIOTRACERS CH_3I AND I_2 THROUGH $Na^{123}I$ SALT

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ABSTRACT

The objective of the present work was to develop, separately, methodology for production of two gaseous tracers through the sodium iodide NaI marked with ^{123}I. Found in the nature in form different, the iodine has been used in diverse works in the area of the industry and health. These two forms of the gaseous iodine, the methyl iodide, CH_3I, and molecular iodine, I_2, are very unstable and volatile in the ambient temperature and presents different problems in clean-up and monitoring systems. The syntheses were processed with sodium iodide (NaI) 1M aqueous solution marked with ^{123}I. The production of gas I_2 was realized with in chlorine acid (HCl) and sodium iodate salt ($NaIO_3$) and the CH_3I was used, the salt of NaI and the reagent $(CH_3)_2SO_4$. The production of gases was initially realized through in unit in glass with an inert material and the purpose was to study the kinetic of reaction and to determine the efficiency of production. The two synthesis occurs in the reaction bottle and after of produced, the gas is stored in the collect bottle that contains a starch solution for fixed the I_2, and in syntheses of CH_3I contains a silver nitrate solution for your fixation. To determine the efficiency of production of gases, analytic tests were realized, where the consumption of iodide ions of the bottle of reaction are measured. The optimization of production of the each gaseous tracer was studied varying parameter as: concentration of iodide, concentration of acid and temperature. After, the syntheses of the radiotracers were realized in the compact unit, having been used as main reagent the salt radiated of sodium iodide, $Na^{123}I$. The transportation of elementary iodine and methyl iodine was studied by a scintillation detector NaI (2 x 2)" positioned in the reaction bottle.

1. INTRODUCTION

In the commercial processes for extracting iodine from natural iodiferous brines, the brine, which in all cases so far know contains at most an extremely small percentage of iodine, is treated with a suitable oxidizing agent, e.g. chlorine, to liberate the iodine in the elemental state. A direct separation from the aqueous medium of the minute amounts of free iodine present by the usual method of settling and filtration is not possible, owing to the fact that such amounts of iodine are considerably below the limit of solubility thereof in the aqueous medium. It is necessary, therefore, to vaporize the iodine by steaming or blowing out with air,

and to recover the vapors by absorption in a suitable liquid medium, usually in an aqueous alkali, or by adsorption upon a suitable solid medium such as active carbon or charcoal. In the case of absorption of iodine in an aqueous alkali, the iodine is obtained in chemically combined form as a mixture of alkali metal iodine and iodate, while in the last mentioned case the iodine may be recovered from the charcoal by leaching with a hot aqueous alkali, whereby owing to the reducing action of the charcoal a solution of iodide may be obtained which is substantially free from iodate. The iodine is recovered in any case, therefore, not as the pure element, but in chemically combined form as the alkali metal iodide or a mixture of the iodide and iodate [1, 2, 3].

2. METHOD USED

The production of the radiotracers, elementary iodine (I_2) and methyl iodide (CH_3I) are realized in the radiotracer laboratory at the Institute of Nuclear Engineering – IEN.

For safety, the first study were realized with the inert salt (NaI) and the last with the radioactive salt ($Na^{123}I$), where were analyzes the production efficiency. A distillation system was used to synthesize the I_2 and CH_3I gases from the inert salt of NaI, as shown in figure 1, besides identification tests and quantification of the iodide ion were done for both tracer ones, as shown in figure 2 (a) and (b). For the syntheses was used one three neck round bottom flask, called reaction vase, where one of the input was added compressed air; other input was introduced the solution of the NaI way dropping funnel 250 mL and in the center neck was used one Allihn condenser. Linked to the condenser were connected three collect vases interlinked through a hose of latex [3].

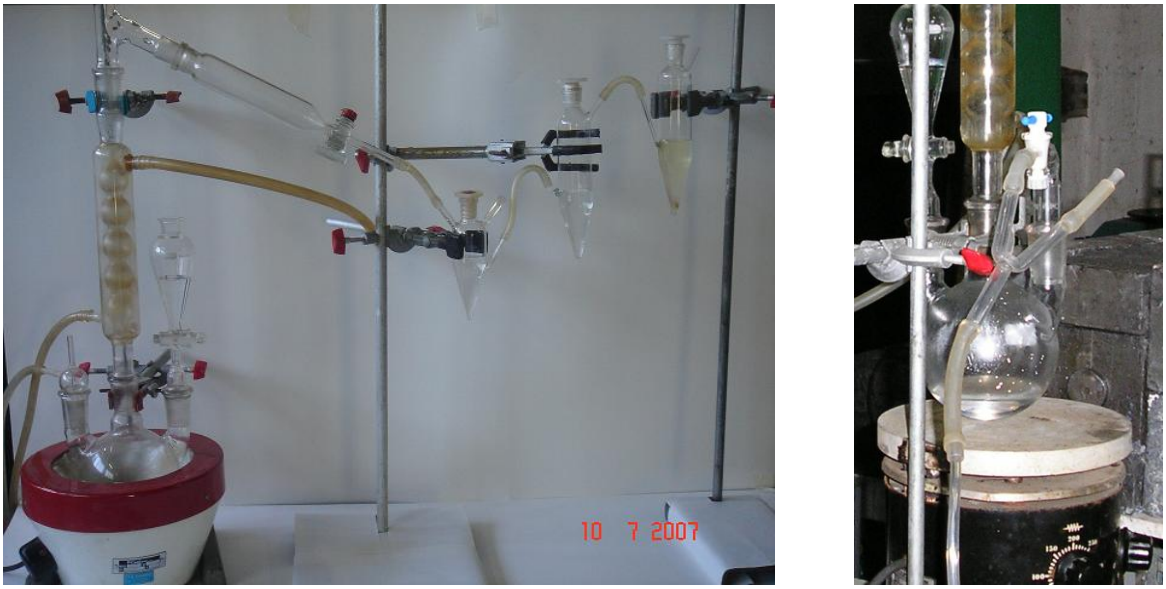

Figure 1. Production system of gases I_2 and CH_3I

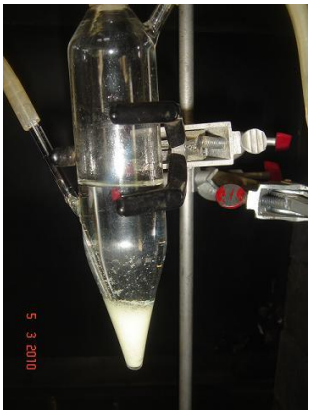

Figure 2. (a) Identification system of gas I_2 (b) Identification system of gas CH_3I.

For the radioactive salt a compact unit of gas production was used, as shown in figure 3. Now, for the tests with the radioactive salt was chosen as radiotracer the ^{123}I ($T_{1/2}$ = 12.9 h e E_γ = 0.159 MeV), in the solid form NaI. The salt was produced way cyclotron at the Institute of Nuclear Engineering (IEN) for the reaction (p, 2n). The activity used in the first production test of the elementary iodine was of 1.4 x 10^8 Bq, and for the production of the methyl iodide the activity employed was of the 2.77 x 10^7 Bq.

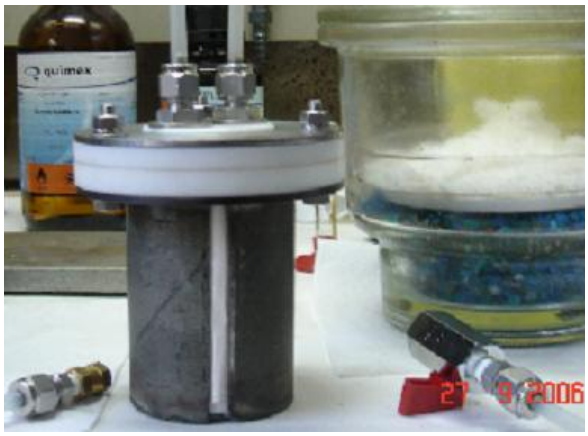

Figure 3. Lateral sight of the compact unit of gas

2.1. Synthesis of the elementary iodine and methyl iodide.

A) Synthesis of the elementary iodine

Among the several synthesis of production of the gas I_2, the synthesis below is more favorable in terms of cost, security and to the laboratory conditions. With a mixture of iodide and iodate simple acidification with chloride acid, will result in precipitating iodine, and if the molecular proportion is in the ratio of five iodides for one iodate, such precipitation by acidification will be quantitative, in accordance with the typical equation 1:

$$5NaI_{(aq)} + NaIO_{3(s)} \xrightarrow{80\ ^\circ C,\ HCl} 3I_{2(g)}\uparrow + 6NaCl_{(aq)} + 3H_2O_{(l)} \qquad (1)$$

If there is a deficiency either of iodate or of iodide as required by the equation 1, this may be made up by suitable addition to the solution prior to acidification [4].

For the synthesis was employed 12.5 mL of a solution of sodium iodide 2 M; 1 g of sodium iodate, exempt sodium iodide; and 10 mL of chlorine acid 3 M. For the test with the inert salt it was evaluated the efficiency of production of elementary iodine of reaction 1.

B) Synthesis of the methyl iodide

The classic synthesis of the methyl iodide was accomplished for the first time in 1835 for Dumas and Peligot [6]. Methyl iodide is formed via the exothermic reaction that occurs when iodine is added to a mixture of methanol with red phosphorus, but the authors inform that the synthesis needs cares, because red phosphorus does ignite in air at temperatures below 260 °C. Therefore was used the synthesis described by Weinland and Schmidt [7]. The production of the methyl iodide was prepared from the reaction of dimethyl sulfate with sodium iodide, as shown in equation 2 [5, 6], below:

$$NaI_{(aq)} + (CH_3)_2SO_{4(l)} \longrightarrow Na(CH_3)SO_{4(aq)} + CH_3I_{(g)} \quad (2)$$

The disadvantage this reaction is in the high cost of the reagent dimethyl sulfate, because it needs to be imported and it needs to have authorization of the armed forces.

C) Identification test

It was necessary the development of methodology for measure of concentration of iodide contained in the solution, and, two tests, independent, were used in the identification of the tracer ones, the first was used as indicator agent a solution of starch, and the second using a solution of $AgNO_3$ [4].

C.1) Identification test of the elementary iodine

The identification test of the elementary iodine was made through a solution of starch as indicator. Starch is often used in chemistry as an indicator for redox titrations where triiodide is present. Starch forms a very dark blue complex with triiodide which can be made by mixing iodine with iodide [4]. However, the complex is not formed if only iodine or only iodide (I^-) is present. The complex is unstable in low concentrations of iodine and highly stable in high concentrations of iodine. The solution of starch was also used as retention agent of the radioactive gas.

C.2) Identification test of the methyl iodide

The employed procedure was the titration by the Farjans method, with $AgNO_3$ as titrant, whose concentration is known with precision and it reacts quantitively with a known solution that contains the iodide ion to be determined [6]. The titrant $AgNO_3$ was standardized, to a 0.97 M concentration, and the eosin was chosen as the acid indicator [3, 5, 8].

In agreement with the equation II.3, the reaction of the alkyl halides with the silver nitrate forms a precipitate of silver halides. For the case of the silver iodide (AgI) the precipitate finely divided acquired a green-yellowish color.

$$RX + AgNO_3 \xrightarrow{ETANOL} AgX_{(s)} + RONO_2 \quad (3)$$

3. DISCUSSION OF RESULTS

3.1. Determination of the Production efficiency of the elementary iodine and methyl iodide

Initially the synthesis was carried through with the inert salt and after studied the behavior and the efficiency of the reaction, the salt was radiated. The necessary quantity of volumes for the execution of the each synthesis was calculated, through the stoichiometric calculation of the chemicals equations 1 and 2. All tests with the inert salt were realized following considerations below:

- The solution of sodium iodide 2 M was used in the two experiments.
- In the titration were used a solution of silver nitrate 0,1 M.
- For determination of the concentration of the (I^-), samples of the reaction vase were collected with volume of 0.5 mL solution each and later diluted for a volume of 10 mL.
- In each sample, 1 mL of the indicator eosina was added and later titranted with the standardized solution of $AgNO_3$ 0.97 M.

A) Synthesis via NaI inert salt of the elementary iodine

The synthesis was processed with 10 mL of chlorine acid (HCl) 3M, 12.5 mL of sodium iodide (NaI) 2 M and 1 g of sodium iodate salt ($NaIO_3$). Being that, first the acid is mixed with the $NaIO_3$, immediately afterwards the NaI is dripped on the mixture that it is being agitated. When the NaI enters in contact with the mixture, has an instantaneous reaction, in which are formed elementary iodine crystals (black color) and also I_2 gas (violet color), as shown in figure 4.

Figure 4. Formation of elementary iodine crystals and also I_2 gas

Depending on the concentration of the NaI it has a greater or minor formation of the precipitated one. The solution is yellowish indicating that it had the formation of a complex of the NaI with the I_2, indicated for NaI_3^-. This chemical species is steady to the ambient

temperature and makes with that the I_2 is fixed. The increase of the temperature has contributed in the release of the gas and also in the kinetic one of the reaction. After produced, the iodine cannot be launched in the atmosphere. Thus a way was developed to hold back it. The produced gas is stored in three collect vases that contain a starch solution (5 g/100 mL water). Another employed test was the observation in the color of the starch that reacts with the I_2, how many more gas is produced, more saturated is the starch solution.

For the synthesis with the inert salt the consumption of present iodide in the reaction vase was studied through of titration. With an automatic pipette, they had been removed, to each 15 minutes, samples with volume of 0.5 mL, diluted for 20 mL of water and placed in test tube. In each sample, 1 mL of the indicator eosin was added. After using a calibrated burette to add the titrant, it is possible to determine the exact amount that has been consumed when the endpoint is reached. The solution changed of color, passing of the color orange for violet.

The first sample of the reaction vase was collected as soon as the synthesis was initiated, being the initial concentration of ions iodide of 2 M. The synthesis was initiated to a temperature of 29 ºC (ambient temperature) e, immediately afterwards, the temperature was raised for 70 ºC.

With the elevation of the temperature, it was observed that the solution of starch of the first vase was in the pink color and that with the time the color changed for light purple, indicating that the iodine transported by the compressed air was kept in the solution of starch.

After 10 minutes (stabilization of the temperature in the reaction vase), a new aliquot was collected, where the concentration of ions iodide was of 1.2 M, indicating that 40% of ions I^- had been transformed into the I_2 gas. In the reaction vase the precipitate black decreased, and in the first retention vase a dark purple color was observed, indicating that the iodine transported by the compressed air was kept in the solution of starch. In the second retention vase was observed a small formation of the purple color.

When the temperature was kept constant around 70 ºC, a new aliquot was collected in t = 20 minutes with a concentration around 0.75 M and production around 62,5%.

This temperature was kept around 20 minutes (t = 40 minutes and t = 60 minutes) and figure 5 show that did not occur consumption of ions I^-, as it is observed by the formation of a small level in the concentration curve. In the reaction vase the solid iodine was decreasing, while the two retention vases were totally saturated and it was necessary to put a third vase to keep the remaining of the present iodine in the reaction vase.

The temperature was raised up to 100 ºC and three aliquot had been collected, in intervals of 10 minutes. A decrease in the concentration of I^- was observed (concentration of 0.15 M of iodide), indicating new production I_2 gas. Later the temperature it was kept constant and the consumption of ions iodide continued to occur more slowly until reaching a constant value (80 minutes of synthesis), indicating that the amount of reagents in the way does not favor more the production of the I_2 gas. The total efficiency of the production of I_2 in the reaction was around 92.5%.

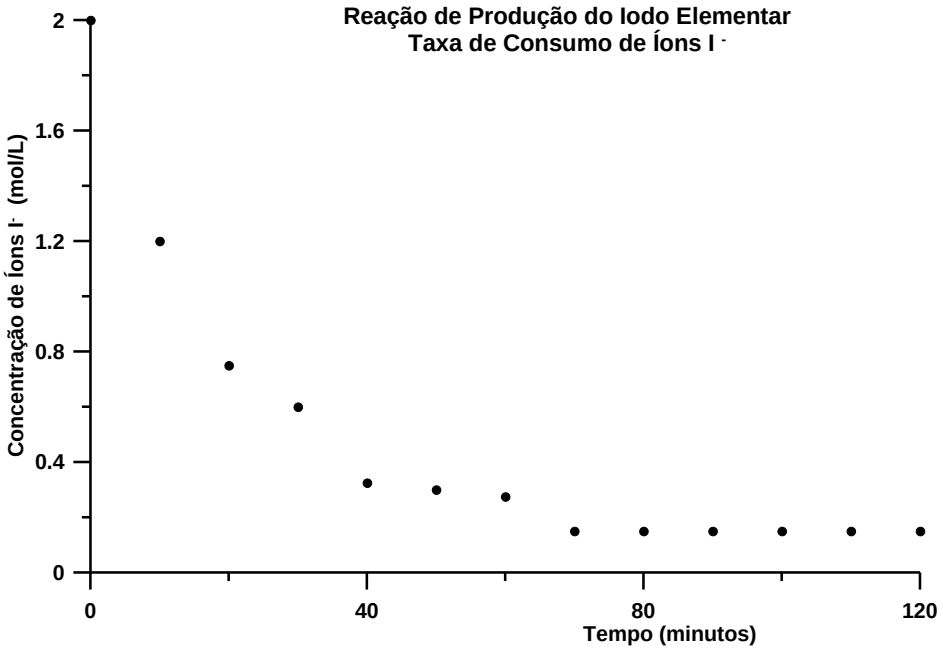

Figure 5. Chemical analysis indicating the rate of consumption of iodide, through the production of the gas I_2.

B) Synthesis via NaI inert salt of the methyl iodide

The production test of the methyl iodide was realized utilizing 6.68 g of NaI and that it was diluted for a volume of 22.3 mL of deionized water forming a solution of NaI 2M. Equal to the previous test, the solution was stocked in a dark flask to protect the action of the light. It was used 4.22 mL of $(CH_3)_2SO_4$, dimethyl sulfate. The two reagents were added in the three neck round bottom flask. In the reaction vase is visible the formation of two phases, the dimethyl sulfate stay in the inferior part and the solution of NaI stay in the superior part, as shown in the figure 6.

Figure 6. Synthesis of the methyl iodide

All synthesis was calculated, through the stoichiometric calculation of the chemicals equations 2. For the retention of the methyl iodide two retention vases were put containing 50 mL of the solution of silver nitrate 1M.

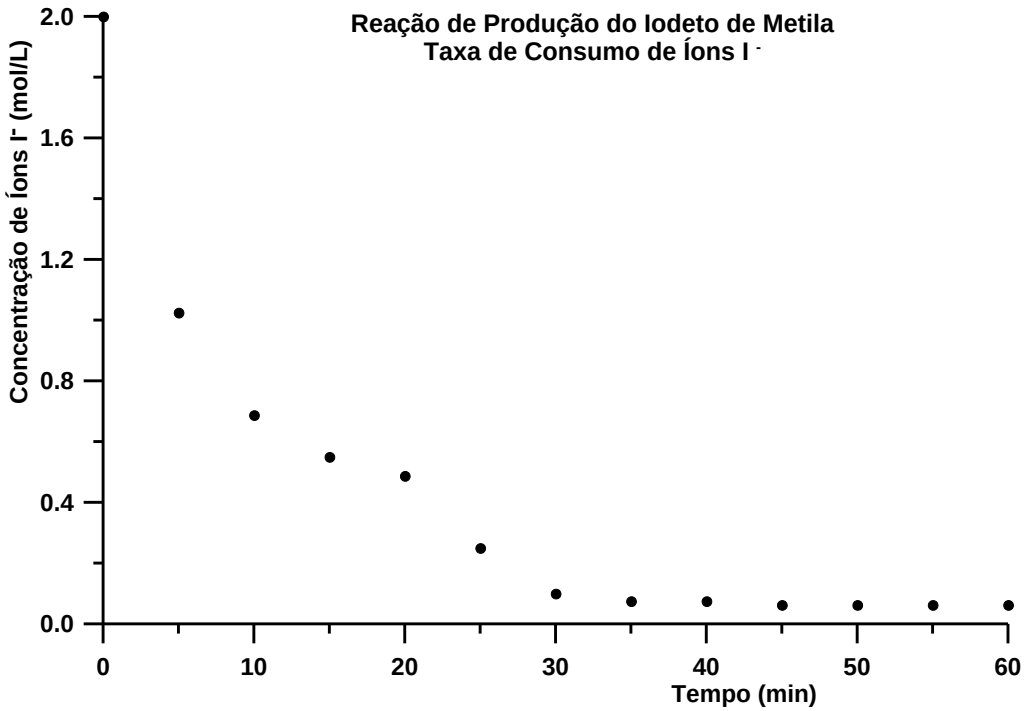

Figure 7. Chemical analysis indicating the rate of consumption of iodide, through the production of the gas CH_3I.

To determine the consumption of the ions iodide into of the reaction vase, it realized a similar procedure to the previous, but the interval of retention of the samples was of 5 minutes, as shown in the figure 7 above.

The synthesis was initiated to a temperature of 26 ºC and the first sample was collected of the reaction vase being the initial concentration of ions iodide of 2 M. After that was used the mixture and the temperature was raised and maintained constant in 70 ºC.

After the increase of the temperature was observed that in the solution of the reaction vase it was milky and soon after the formation of some bubbles was observed, the liberation of the gas CH_3I. In the second collect in t = 5 minutes was observed a great variation in the iodide concentration, 50% of the gas CH_3I was formed and 50% of the (I^-) it is in solution. The precipitate formed in the reaction vase was dissolved and in the first retention vase the solution of the silver nitrate quickly reacted forming a precipitate green-yellowish.

Among t = 10 minutes and t = 20 minutes, a part of the gas was removed and kept in the first retention vase. After t = 20 minutes the second retention vase presented the formation of the precipitate of AgI. The concentration of ions iodide was of 0.48 M, indicating the production of the 75% of the CH_3I.

In the figure 7 was observed that among t = 30 minutes and t = 45 minutes, the quantity of (I^-) into of reaction vase decreasing slowly, going of 0.1 M to the final concentration of 0.065 M. The total efficiency of the production of CH_3I in the reaction was around 97%.

3.2. Reaction via radioactive salt

Complementing the studies of the productions of the gases I_2 and CH_3I, two tests, independents, were realized with salt NaI previously irradiated in Cyclotron. The tests were equals to the not irradiated salt above shown.

To register the efficiency of production of the gaseous CH_3I e I_2 was used one NaI (2 x 2)" scintillation detector positioned to 10 centimeters of the lateral of the compact unit, where this was shielded by lead walls with 5 cm of thickness, where the collimator had an opening of 0.5 cm of diameter.

A) Synthesis of the elementary iodine via NaI irradiated salt

Two tests had been carried through in the compact unit, the first one were placed a concentration of NaI 0.075 M and the last was carried through with a concentration of NaI 0.1 M. The response curve of detector, figure 8 and 9, represents the production and transportation of the I_2 gas. Each curve was normalized and the initial temperature was around 32 ºC. Variations were observed in both response curves for the total time of the synthesis, these oscillations are due to the intense movement of I_2 cloud in the reaction vase.

The first synthesis occurred after the time of acquisition of 35 minutes, having been the interval each counting of 1 second. It was observed that it did not have removal of radioactive material, because did not have inclination of the curve. After of 20 minutes of synthesis the temperature was increased for 90 ºC, after 10 mL of acid 1 M had been added and exactly thus it did not have variation in the format of the curve. The confirmation was through the starch solution, therefore no variation in the color did not occur.

After observed that it did not have extraction of I_2, then the concentration of NaI was increased for 0.1 M. The contour conditions had been the same ones used in the last test.

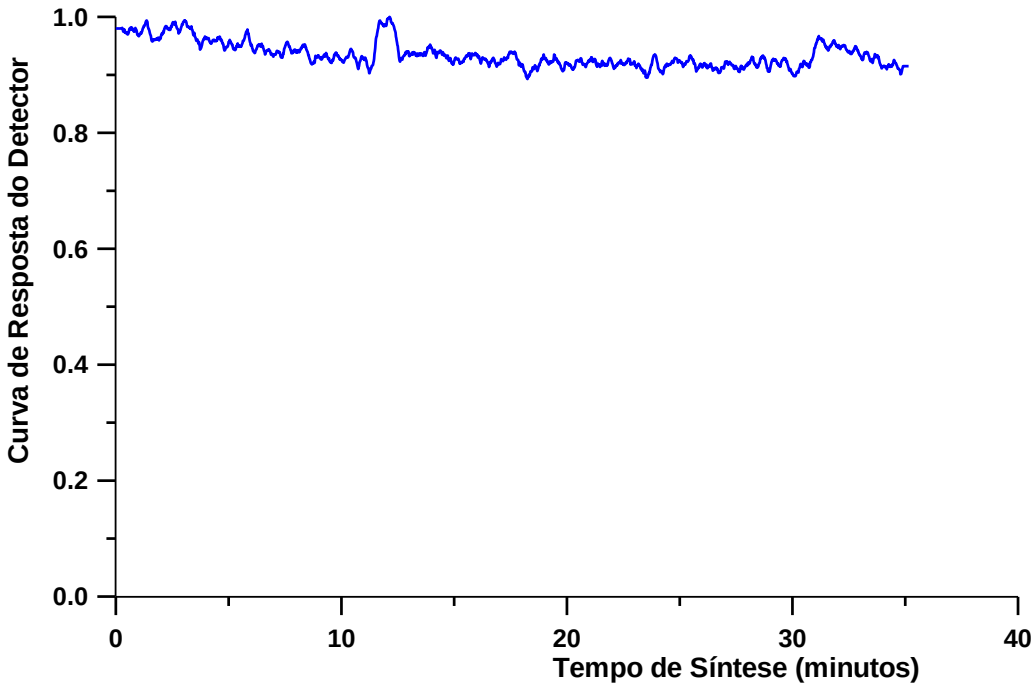

Figure 8. Response curve of detector for first test (concentration of NaI 0,075 M).

As presented in figure 9, around 25 minutes, the temperature was approximately in 70ºC, and the first injection of the I_2 in the collect bottle occurs. So that the extraction is maximum was passed air compressed in a period of 5 minutes and after close the valve. In the response curve was observed a great removal of I_2, verified through the great inclination of the curve. The unit again was pressurized and in approximately t = 40 minutes, a new injection was effected, being registered a new removal of radioactive material, due to the increase in temperature for 81 ºC. Between t = 50 minutes and t = 100 minutes, occur a great variation in the consumption of the material and the temperature oscillated between 81 ºC and 85 ºC. After 100 minutes it was not observed any removal of the gas I_2. The variations in temperature showed that the material was removed from the reaction vase and the total efficiency of the extraction of I_2 was of around 83.3 %.

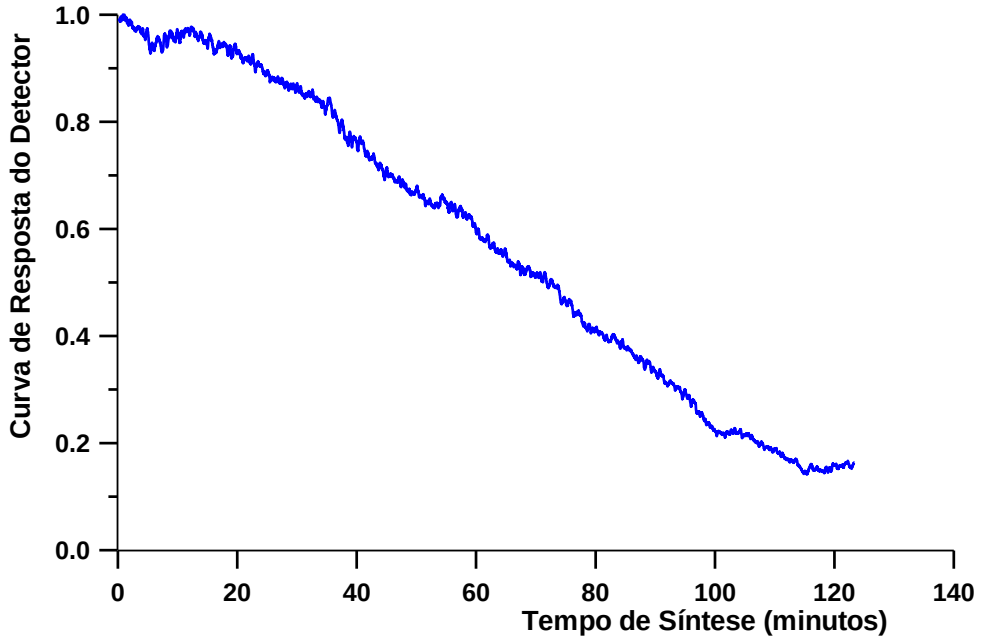

Figure 9. Response curve of detector for last test (concentration of NaI 0.1 M).

B) Synthesis of the methyl iodide via NaI irradiated salt

The radiochemistry test to determine the efficiency of extraction of the methyl iodide in the compact unit was realized using the same quantity of the reagents employed in the test without the activation of the ^{123}I. The data were registered through of the NaI (2 x 2)" scintillation detector and transferred for to acquisition system that was programmed to register the signals to every 1 second. The response curve of detector was showed in the figure 10, where the data were normalized in relation to the largest signal registered being possible to determine the rate of extraction of the methyl iodide gas produced in the compact unit.

After the injection of the solution of the salt, it was realized the acquisition and soon after put the temperature. Until the stabilization of the temperature, the unit was pressurized and after 5 minutes the first liberation of the gas was realized and a great removal of the radiotracer was observed, being around 60% of all material activated contained in the compact unit. After it was passed compressed air for three minutes and the methyl iodide was kept in the collection vase containing solution of silver nitrate 1 M.

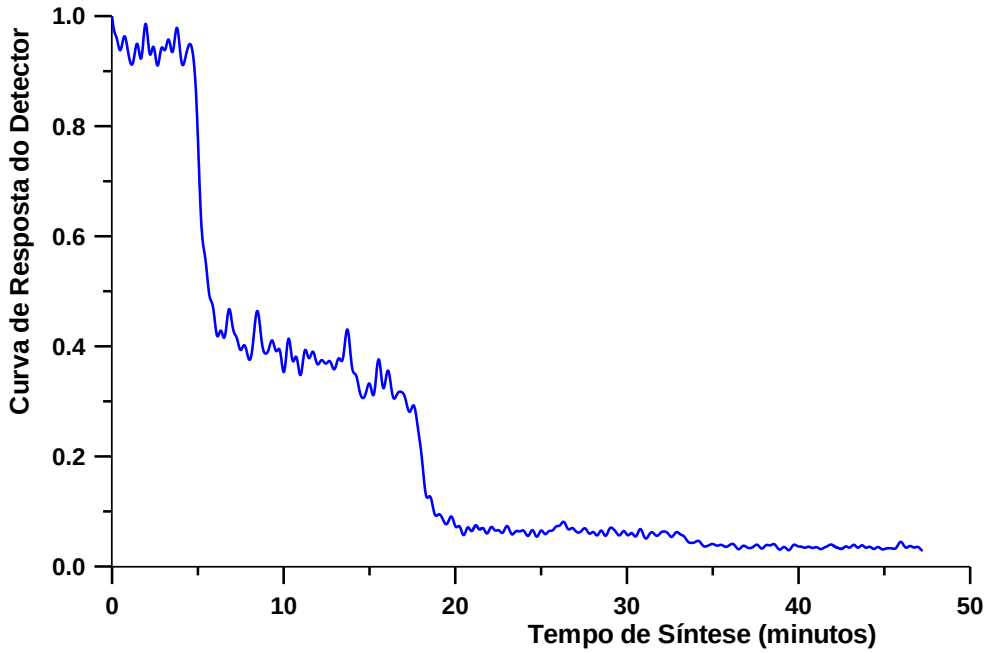

Figure 10. Response curve of detector for test of the methyl iodide using NaI irradiated

The unit was pressurized again by 10 minutes and in t = 15 minutes and t = 18 minutes two injections were realized. That occurred because the valve was hardened, but even so that variation was observed. In the second injection one greater quantity was removed reaching 92% of extraction and in the collection vase were formed more precipitate finely divided of the green-yellowish color, indicating to be silver iodide. The unit was pressurized by 15 minutes and around t = 33 minutes the third injection was realized, where it was observed that the removal of the gas was not significant. Therefore, the efficiency of extraction of the methyl iodide using the compact unit was of 97%.

4. CONCLUSIONS

In accordance with the reactions of the synthesis, one can conclude that a number of factors influence and others no influence the production of the CH_3I gas and I_2 gas, such as:

- Temperature – for the two syntheses increase in production is directly dependent on the increase in temperature;
- The quantity of reagents used:
    - The excess of HCl for the reaction of production of the elementary iodine favors the removal.
    - For the test of the elementary iodine is important to work with pure reagents, because the contamination of the same ones does with that the income is reduced or the synthesis doesn't happen.
    - The quantity of reagents for the two syntheses should be in agreement with the chemical equation.

- It was observed in the radiochemistry test for production of the elementary iodine that starting from a certain quantity of reagents (0.075 M of NaI), is unviable the realization of the synthesis, because the quantity of produced gas is quite small and it doesn't tend pressure to be extracted.

- The retention means, as much the solution of starch as the solution of silver nitrate 1 M were efficient in the collection of the gas produced.

- Some of the advantages of the process, such as the fact that the reagents are easily acquired on the local market at a low cost, and that the radioactive tracer can be used in diverse works in the area of the industry and health due to its ease of production, identification and measurement.

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